HEAT INSULATING MATERIALS

CONTROL OF PORIZATION IN LIQUID GLASS BASED THERMOFOAM SILICATE ARTICLES

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It is shown that the unified equation of thermodynamics should be used when attempting to control the preparation of liquid-glass mixtures and their porization to obtain thermofoam silicate articles. The main factors influencing the porization process and the final properties of the thermofoam silicate articles are determined. The characteristics of the heat insulating materials using basalt flakes are indicated.

Key words: liquid glass, filler, basalt flakes, thermal porization, thermofoam silicate articles.

Liquid glass, a typical nanodispersed system, possesses the unique capability of creating when heated to $150 – 450°C$ solid inorganic foam with density to 50 kg/cm^3. This is due to its structure and composition and the high dispersity of the molecular formations in the solid phase. If the process of obtaining such a foam can be conducted in a closed volume of the forming space, then thermofoam silicate (TFS) heat-insulating articles with a prescribed shape and size, density $100 – 250$ kg/m^3, and thermal conductivity $0.05 – 0.08$ W/(m · K) can be obtained on the basis of such a foam.

The seeming outward simplicity of this process conceals complicated technological problems, which are due to, first and foremost, the high moisture content of the liquid glass. For example, the initial sodium liquid glass with density 1450 kg/m^3 and modulus 3 contains about 55%[4] liquid phase and 45% solid phase. To effectuate the porization process practically all of the free water must be removed from the glass and only the structural water, which is removed at temperatures above $110°$, must be allowed to remain. On heating, the structural water at first dilutes the xerogel forming after the free water has been removed, transforms it into a pyroplastic state and with further heating, resulting a vapor-like state, forms a dispersed phase of the system in the form of fine spherical bubbles separated by interpore barriers of a solid dispersed medium. The vapor formation completes the work performed during the expansion of the system as it passes from a plastic-viscous into a solid state.

The objective of the present work is to validate methods for controlling the porization of liquid glass on the basis of a thermodynamic approach at the stage of preparation of the liquid-glass composition (LGC) and at the stage of its porization under thermal heating.

The critical stage of the technological process of obtaining TFS articles on the basis of liquid glass is the preparation of the initial LGC, which must possess high porization capability when heated thermally. When fillers and additives are introduced into the liquid glass its porization capacity decreases because of a decrease of the free energy of the system, which is very sensitive to the amount of additives introduced and the degree to which the liquid glass decomposes.

The diversity of mineral fillers and chemical additives suggests an empirical diversity of LGC compositions. Helpful information about the mechanism by which the mineral fillers and chemical additives influence the properties of LGC at the preparation stage and during porization can be obtained by analyzing the unified equation of the first and second laws of thermodynamics:

$$\Delta G = P\Delta V + \sigma\Delta s + \mu\Delta n + \varphi\Delta q - T\Delta S = \Delta H - T\Delta S,$$

where ΔG is the Gibbs free energy, whose magnitude and sign can be used to predict the intensity and direction of the change of the energy state of a dispersed system; $P\Delta V$ is the work performed by the system during a change of volume or energy, required for this change; $\sigma\Delta s$ is the work performed

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by the system during the formation of a new surface, or energy released or absorbed during this change; $\mu\Delta n$ is the work performed by the system or absorbed when new chemical compounds are formed or matter in the system undergoes changes and mutual transformations as well as changes of its phase composition; $\varphi\Delta q$ is the work performed by the system accompanying a change of its electric potential and amount of electricity during a change of the ionic composition of the liquid or solid phase, formation of a new surface, during dispersing and viscoplastic flow of the solid phase; $T\Delta S$ is the entropy factor, characterizing the change in the degree of disorder in the experimental system under energetic action, including heating; and, ΔH is the enthalpy factor of the system, consisting of four possible and intercoupled energetic actions on the system.

As a result of the high dispersity of its solid phase, liquid glass is in a metastable, unstable state, and any external energetic actions give rise to quite strong changes of its composition and properties, right up to complete destruction and degradation.

Mineral fillers or additions of chemical substances used in the preparation of LGC give rise to an individual reaction of the liquid glass to each additive that is introduced. Finely dispersed mineral fillers introduced into LGC in amounts above 8 – 10%, adsorbing into their surface ions of the liquid glass or binding free-water dipoles, either give rise to gel formation in the liquid glass or thin the mixture [1, 2]. The nature, dispersity, and amount of filler introduced have a decisive effect on the development of gel-formation processes, during which the LGC must acquire the solid-like viscoplastic state required for subsequent granulation of the mixture in auger granulators.

When selecting fillers one must keep in mind that gel formation in liquid glass occurs with the removal of free water during drying, adsorption binding, and hydration, as a result of which the concentration of the solid phase increases because of depletion of silicate ions in the more extended polymer groupings without detachment alkali-metal ions by these structures.

When a large quantity of finely dispersed filler is introduced its surface energy is sufficient for molecules of structural water and alkali-metal cations to be adsorbed, which destroys the liquid glass and forms a loose silica gel mass. The latter has the effect of decreasing the entropy, dispersity, and surface energy of the system, which drives it toward equilibrium, and thermal action at comparatively low porization temperatures is incapable of converting this system into a developing system.

Thinning of the mixture with the introduction of mineral fillers is due to the specific nature of the surface properties, sign, and magnitude of the charge of their particles which are capable of substantially changing the electric potential of the entire system and the charge of its solid-phase particles. Thinning of the LGC is accompanied by some destruction of the liquid glass as a result of charge transfer and neutraliza-

tion of the surface charge of the newly formed dispersed phase and their agglomeration into small neutral aggregates, which together with the dispersed medium form an unstable, stratifying suspension.

Such a suspension can be used in a technological process only after it has undergone liquid granulation in salt solutions, for example, calcium or aluminum chlorides [3]. An external chemical action on the suspension with granulation is manifested as an increase of the concentration of the solid phase in granules as well as redistribution of the components of the suspension between granules and the salt solution.

If the introduction of mineral fillers into liquid glass has an electrophysical effect on the system, initiating work performed by the system to decrease the surface energy of the solid phase, then when chemical additives are introduced various types of chemical reactions (neutralization, substitution, exchange) occur in the system together with these actions. The desirability of introducing chemical additives into the liquid glass is predetermined by the need to regulate certain final properties of the TFS articles. The degree of completion of these reactions depends on the amount of a chemical addition, and for a stoichiometric ratio of the reaction components complete destruction of the liquid glass can be attained. For example, calcium hydrosilicates, silica gel, and sodium chloride form when calcium chloride interacts with liquid glass. A mechanical mixture of these reaction products completely exhausts the capability of transferring into a pseudopyroplastic state and undergoing porization on heating.

When liquid glass comes into contact with calcium chloride, which occurs during liquid state granulation, 0.2 – 2.0% calcium chloride is drawn into the reaction volume, but the reaction products formed in the surfaces of the granules are entirely sufficient to increase, for example, the strength of the finished articles without a large decrease of the porization capacity of the liquid glass.

Introducing a combined additive, containing mineral filler and a chemical addition in the optimal quantitative ratio, into the liquid glass composition also makes it possible to obtain an LGC with high porization capacity. Depending on their composition and quantity combined additives make it possible to regulate gel formation and porization as well as to act purposefully on the processes resulting in the formation of the porous structure, strength, and water resistance of the articles.

Gel formation performed using additives and fillers decreases the free energy of the prepared system (LGC). This is manifested as a decrease of the enthalpy of the system as a result of particle sizing increasing from 3 – 10 nm to 10 – 50 µm, a change of the chemical potential, component composition of the system, and a change of the electric potential as a result of charge exchange or charge neutralization of the particles.

The intensity of the thermal porization of the initial LGC is predetermined by the mandatory presence of intact liquid glass in the composition. Power energetic action during heat-

ing of LGC transfers it from the stationary state into a dynamic one, which develops because of the presence in the initial LGC of excess free charge that plays the role of a primary energy pulse. Subsequent development of the porization process is accompanied by a change of the phase composition of the system, its enthalpy and entropy factors, whose total value gives a negative value of the Gibbs free energy.

The enthalpy factor (ΔH) changes with porization because the system performs the following types of work:

change of volume of the system during evaporation of liquid;

change of volume of the pseudopyroplastic solid phase;

formation of a new surface and increase of the surface tension of the solid phase;

change of the chemical potential, phase, and component compositions of the system as it transitions from the pyroplastic into the solid state;

charge transfer during viscoplastic flow of matter and increase of the electric field strength accompanying the formation of an extended surface of the pore space.

The entropy factor ($T\Delta S$) increases with porization because of not only a sharp increase of the temperature but also a positive increase of the entropy as the volume of the system increases together with the total surface area of the pore structure with the thickness of the interpore barriers decreasing. An increase of the disorder in the porized system makes the system more stable.

The applicability of the principles given above for controlling the technology for preparation of LGC and its porization can be illustrated for the example of basaltic flakes (BF) used as a mineral filler, which is obtained when a basalt melt is dispersed. BF consists of flakes with diameter 0.25 – 3.00 mm and predominant thickness 1 μm. The true density of BF is 2450 kg/m^3. For BF bulk density 100 kg/m^3 the porosity of the layer is 96%, and the volume content of the solid phase is 4%. As a result of the composition, structure, and high specific surface area BF possesses high water retention (6 g water per 1 g flake). The glassy state of the flakes, unusual surface properties, capability of acquiring a large electric potential, chemical inertness with respect to the liquid glass were the main arguments for using BF.

When the LGC was prepared the flakes were introduced in the amounts 3, 5, 7, and 10%. The dispersed reinforcement of the inorganic foam by the flakes gives a more uniform and stronger structure of the heat-insulating article. The effect of the amount of BF introduced on the properties of the articles is reflected in Table 1.

It was determined that the maximum amount of the BF introduced is 7%, for which the volume amounts of the mixed components are equal. With 10% BF the flake volume is 1.5 times greater than the volume of the liquid glass and it is difficult to mix the components, but spontaneous densification of the mixture and water separation are observed after some time. This is an indication of a transition of the pre-

TABLE 1.

Indicator	Mass content of basaltic flakes in LGC, %			
	0	3	5	7
Density, kg/m^3	100	200	300	450
Compression strength, MPa	0.15	0.45	1.08	1.52
Thermal conductivity, W/(m · K)	0.052	0.067	0.083	0.122

* For 10% content of flaked filler the mixture is difficult to mix, and destruction of the liquid glass and water separation are observed.

pared system (LGC) into a stable equilibrium state with a minimum store of free energy as a result of almost complete destruction of the liquid glass occurs. When this mixture is heated to 450°C densification is observed instead of the expected expansion; this confirms the fact that the liquid glass is destroyed. In addition, adhesion between the flakes and foamed mass decreases when such mixtures undergo porization.

At the LGC preparation stage the flaked filler binds the free water first, but slightly later, as a result of the change of the electric potential and the charge of the particles and compression of the electric double layer, free water reappears and thins the mixture. At this stage the electrophysical action, which does not give rise to large volume and surface changes in the system, predominates. The entropy factor at this stage also does not have an appreciable effect on the properties of the mixture. For this reason, to impart a solid-like technological state to the mixture it is necessary to apply a chemical action to the system by introducing into the mixture, for example, calcium chloride or, in the case of liquid granulation, a mixture of liquid glass and flakes in a saturated solution of this salt. The chemical additions stimulate a change of the surface energy of the system by increasing the particle size as changing the ratio between the solid and liquid phases by transferring part of the free water of the mixture into a chemically bound, solid-like state.

In the process of porization of LGC the presence of flakes in the mixture plays an extremely important role in the formation of a uniform porous structure in articles. When the LGC transitions into a pyroplastic state the flakes are incorporated into the mass adhesively and their presence smoothes the force field of viscoplastic flow and the rate of formation of pores and interpore barriers. During porization the enthalpy and entropy factors have essentially equivalent effects and are interdependent.

In summary, at the stage of preparation of the LGC and at the porization stage the transition of the system from the initial into the final state is accompanied by work performed by chemical or physical-chemical processes. For this reason, in the case of control by means of the formation of porous structures based on liquid glass a validated choice of the form and intensity of the external energetic action (composi-

tion, nature, and dispersity of the filler, form of the chemical additives) must be made and the influence of these actions on the direction of the physical – chemical processes must be analyzed. Purposeful control of these processes is the main direction for forming porous structure with prescribed properties.

Applying these approaches to the control of thermal porization processes we obtained heat-insulating materials with strength 1.5 MPa and density 300 kg/m^3 based on liquid glass using basaltic flakes.

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